

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Mobil Composition of Matter Number 41

Mobil Composition of Matter number 41 (MCM-41) used in this research project was supplied by the department of Chemical Engineering and Materials Science, the University of Oklahoma. According to the preparation procedure to obtain siliceous MCM-41, 190 g. of 25 wt% aqueous solution of $C_{16}H_3(CH_3)_3NBr$ (hexadecyltrimethylammonium bromide, CTAB) was mixed with stirring with 58 g of 25 wt.% tetramethylammonium hydroxide. The mixed solution was then added into the solution containing 25 g. of HiSil-915 (PPG Industries Inc.) and 100 g. of tetramethylammonium silicate (10 wt% silica; ratio of tetramethylammonium to silica is 0.5). The mixture was mixed well for about 20 minutes. The prepared solution was placed in a PARR reactor and heated at 150 °C for 24 hours at autogeneous pressure. The solution was taken out and quenched to room temperature (25 °C). The solution was filtered to obtain the solid product. The filtered solid was continually washed with running water for 3 days. Then it was dried at ambient air. Finally, this solid product was calcined at 580 °C for 7 hours in static air. The characterization of this MCM-41 indicates that it has mesopore size distribution at approximately 36 Å ($\pm 2\text{Å}$) from BJH method and surface area of approximately 1005 m² /g.

3.1.2 Silica

The precipitated silica (Hi-Sil 255) used in this study was manufactured by PPG-Siam Silica Co., Ltd. (Rayong, Thailand) and it has the surface area of 170 m² /g.

3.1.3 Surfactants

Five cationic surfactants were used: Octyltrimethylammonium bromide, Decyltrimethylammonium bromide, Dodecyltrimethylammonium bromide, Tetradecyltrimethylammonium bromide and Cetyltrimethylammonium bromide (CTAB). All of the surfactants have a purity of 98 %. Octyltrimethylammonium bromide and Decyltrimethylammonium bromide were obtained from TCI Tokyo Kasei. Dodecyltrimethylammonium bromide, Tetradecyltrimethylammonium Bromide and Cetyltrimethylammonium bromide were received from FLUKA. All the chemicals were used without further purification. The chemical structures of the studied surfactants are shown in Table 3.1.

Table 3.1 Chemical structures of cationic surfactants

Chemical Name	Formula
Octyltrimethylammonium bromide	CH ₃ (CH ₂) ₇ N(CH ₃) ₃ Br
Decyltrimethylammonium bromide	CH ₃ (CH ₂) ₉ N(CH ₃) ₃ Br
Dodecyltrimethylammonium bromide	CH ₃ (CH ₂) ₁₁ N(CH ₃) ₃ Br
Tetradecyltrimethylammonium bromide	CH ₃ (CH ₂) ₁₃ N(CH ₃) ₃ Br
Cetyltrimethylammonium bromide	CH ₃ (CH ₂) ₁₅ N(CH ₃) ₃ Br

3.2 Experimental Procedures

The stock solutions of 1 M of each surfactant were prepared and diluted to various desired concentrations. MCM-41 (0.1 g.) as an adsorbate, was put into a series of screw top test tubes with a PTFE lined cap. Each test tube contained 25 ml with the various surfactant concentrations. The test tubes were capped, sealed with paraffin and placed in a shaking water bath at 30^o C. The test tubes were shaken at a slow speed once a day for the required adsorption days which depended on type of the surfactant (the technique about how to figure out the required adsorption days for each surfactant will be discussed later). The suspension was then poured into a centrifuge tube. The pH of the suspension was measured by pH meter (Benchtop H/ISE Meter, Model 420 Å with Triode pH electrode Model 91-57BN) before centrifuging and the pH was found approximately 5. The suspension was centrifuged 3 times by using a ALC 4236 CENTRIFUGE at 4500 rpm each time for 1.5 hour, to remove suspended particles of silica. The supernatants of the samples were separated from the precipitated solid by using disposable pipettes. The supernatants were then filtered through membrane filter (Gelman science Membrane Filter, Model FP-450 13 mm dia. 0.45 µm).

The equilibrium concentrations of each surfactant were determined by High Performance Liquid Chromatography (HPLC) (Hewlett Packard series 1050) and a conductivity detector (All tech, Model: Lambda 16), and HPLC Software (HPLC 2D Chemstation Rev. A.03.02 Hewlett Packard 1990-1995). The HPLC column was a 3.9x150 mm. Nova-Pak C18 reverse-phase column (Waters Division of Millipore, Millipore Corporation, Milford, MA). The mobile phase solvent for all five cationic surfactants was 10%, HPLC grade methanol (Ajax Chemical, Australia) and 90% deionized water for approximately 1.5 minutes to remove impurities and salts then switch to 90%

methanol and 10% deionized water for 1.5 to 3 minutes to elute analyte. The flow rate of the mobile phase solvent is 1.5 ml/min. The sensitivity of the detector at high surfactant concentrations, it was adjusted to about 100 μ S and for low surfactant concentrations was about 5 μ S to get the sharpest desired peak. All above procedures were repeated for silica adsorption but 1 g silica was used. In each experiment, blank solutions were used to correct for background interferences.

For the method to figure out the required adsorption days for each surfactant on MCM-41 and silica, in this research, 62,000 μ m 25 ml of each surfactant solution was added to MCM-41 (0.1 g.) and silica (1 g.) in a screw top test tube separately and shaken in a shaking water bath at 30^o C. The test tubes were shaken once a day for approximately 5 hours. After that, the suspension was poured into a centrifuge tube. The suspension was centrifuged 2 times by ALC 4236 CENTRIFUGE at 4500 rpm, for 1.5 hours, to remove particles of solid. Part of the supernatant was separated from the solid by disposable pipette and transferred to find the concentration by HPLC. Allow the rest suspension to be adsorbed and repeated all above procedures everyday until the supernatant concentration reached equilibrium (constant concentration). The number of days required for each surfactants adsorption to be adsorbed on MCM-41 and silica could be read out by plotting a graph between surfactant concentration (μ m) versus day adsorbed.